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[54] **N-SUBSTITUTED
CARBOXYLOXYALKYLPYRROLE
INSECTICIDAL, ACARICIDAL AND
MOLLUSCICIDAL AGENTS**

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[51] Int. Cl.⁵ **A61K 31/40; C07D 207/34;
C07D 207/36; C07D 207/42**

[52] U.S. Cl. **514/427; 514/423;
514/424; 514/425; 548/537; 548/543; 548/544;
548/562**

[58] Field of Search **548/562; 514/427**

[56] **References Cited**

U.S. PATENT DOCUMENTS

5,157,047 10/1992 Kamhi et al. 514/423

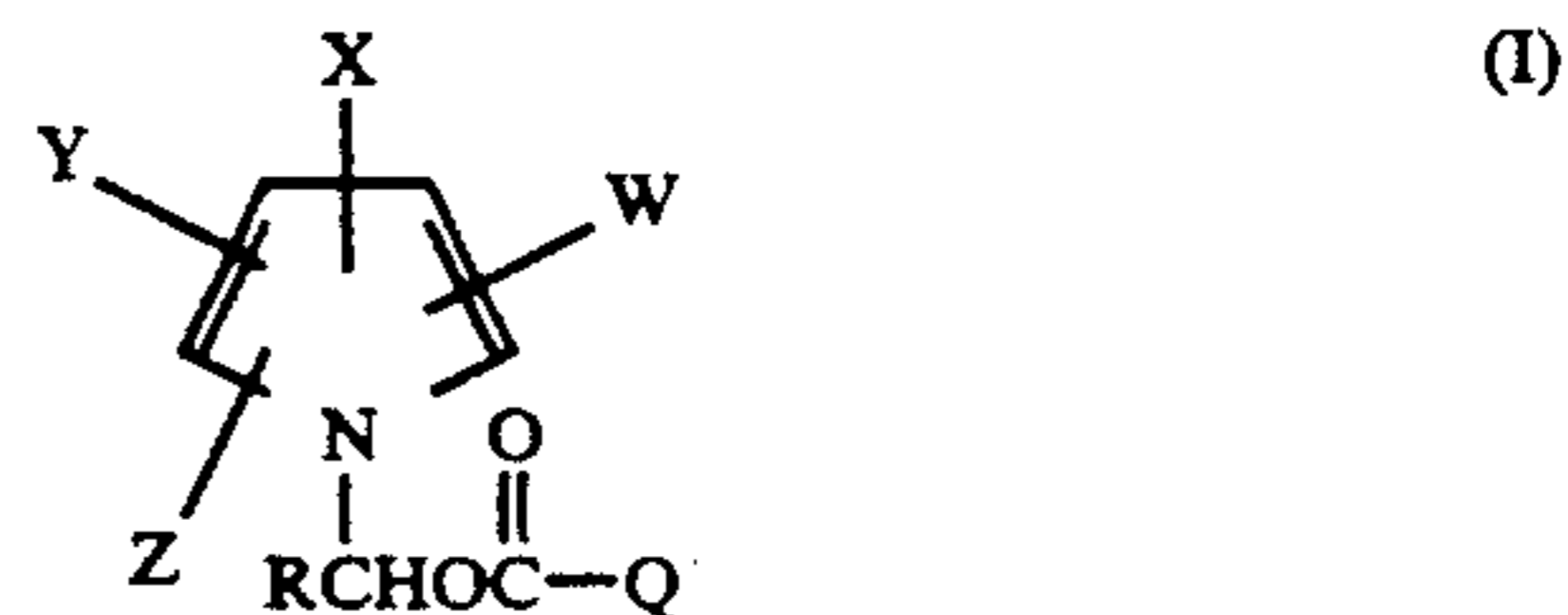
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[57] **ABSTRACT**

There are provided N-substituted carbonyloxyalkylpyrrole compounds of formula I



and their use for the control of insects, acarina and mollusks. Further provided are compositions and methods comprising those compounds for the protection of plants from attack by insects, acarina and mollusks.

24 Claims, No Drawings

**N-SUBSTITUTED
CARBOXYLOXYALKYLPYRROLE
INSECTICIDAL, ACARICIDAL AND
MOLLUSCICIDAL AGENTS**

BACKGROUND OF THE INVENTION

Insects, acarina and mollusks destroy growing and harvested crops. In the United States alone, agronomic crops must compete with thousands of insect and acarid species. In particular, tobacco budworms, southern armyworms, two-spotted spider mites and slugs are especially devastating to crops.

Tobacco budworms cause tremendous economic losses in agronomic crops. In particular, budworms devastate cotton crops by feeding on green bolls. Control of budworms is complicated by their resistance to many common insecticides, including organophosphates, carbamates and pyrethroids. Also, budworm larvae are difficult to control with currently available insecticides once they reach the third instar.

Two-spotted spider mites attack many plant species, raspberry plants for example, by removing sap from leaves. When raspberry plants are heavily infested, canes and leaves become stunted. With a severe infestation, fruiting canes are damaged, resulting in reduced yield and fruit quality.

In spite of the commercial insecticides, acaricides and molluscicides available today, damage to crops, both growing and harvested, caused by insects, acarina and mollusks still occurs. Accordingly, there is ongoing research to create new and more effective insecticides, acaricides and molluscicides.

Certain pyrrole compounds are known to possess insecticidal, acaricidal and/or molluscicidal activity (see, e.g., U.S. Pat. No. 5,157,047 and U.S. patent application Ser. Nos. 392,495 filed on Aug. 11, 1989; 621,162 filed on Nov. 30, 1990; 776,967 filed on Oct. 15, 1991; 795,407 filed on Nov. 20, 1991; 803,289 filed on Dec. 4, 1991; and 971,025 filed on Nov. 3, 1992). However, none of the pyrroles disclosed in those patent applications are within the scope of the present invention.

It is therefore an object of the present invention to provide N-substituted carbonyloxyalkylpyrrole compounds which are highly effective for controlling insects, acarine and mollusks.

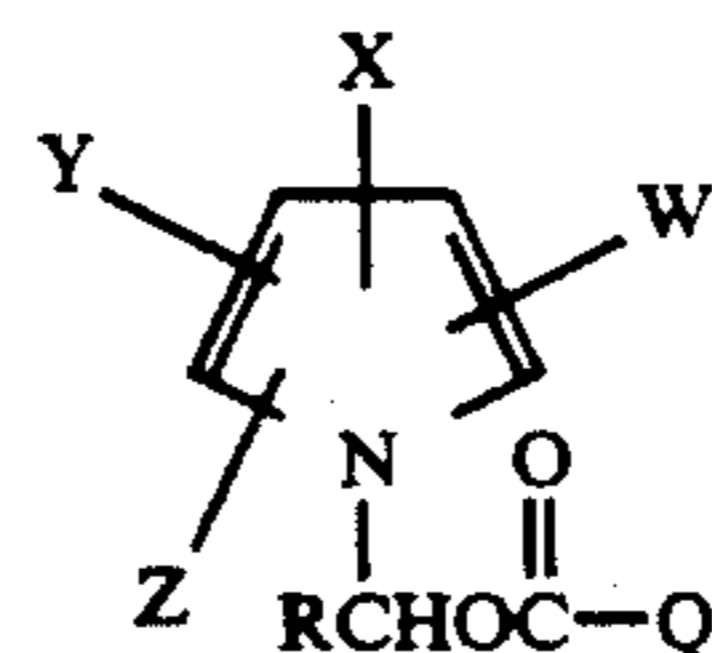
It is also an object of the present invention to provide a method for protecting growing plants from attack by insects, acarina and mollusks by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally, acaricidally or molluscicidally effective amount of an N-substituted carbonyloxyalkylpyrrole compound.

These and other objects of the present invention will become more apparent from the detailed description thereof set forth below.

SUMMARY OF THE INVENTION

The present invention describes N-substituted carbonyloxyalkylpyrrole compounds which are useful as insecticidal, acaricidal and molluscicidal agents for the control of insects, acarina and mollusks and for the protection of plants from attack by insects, acarina and mollusks.

The N-substituted carbonyloxyalkylpyrrole compounds of the present invention have the following structural formula I:



(I)

wherein

W is CN, NO₂, S(O)_nCF₂R₁ or



R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

n is an integer of 0, 1 or 2;

R₂ and R₃ are each independently hydrogen,

C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF₃, CN, NO, S(O)_nCF₂R₁ or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is halogen, CF₃ or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF₃;

R is hydrogen or C₁-C₄ alkyl;

Q is

C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups,

C₂-C₆ alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms,

CR₄R₅C(O)R₆, or

CR₄R₅C(O)A;

R₄ and R₅ are each independently hydrogen,

C₁-C₆ alkyl optionally substituted with one or more halogen atoms,

C₁-C₆ alkoxy optionally substituted with one or more halogen atoms,

C₁-C₆ alkylthio optionally substituted with one or more halogen atoms,

phenyl optionally substituted with one or more halogen atoms,
 CN groups,
 NO₂ groups,
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms, or
 when R₄ and R₅ are taken together with the atom to which they are attached may form a C₃-C₆ cycloalkyl group optionally substituted with one to three C₁-C₄ alkyl groups, C-C₆ alkenyl groups of phenyl groups;

R₆ is

C₁-C₄ alkyl or
 phenyl optionally substituted with one or more halogen atoms,
 CN groups,
 NO₂ groups,
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

A is OR₆ or NR₇R₈; and

R₇ and R₈ are each independently hydrogen or C₁-C₄ alkyl.

This invention also relates to compositions containing those compounds and methods for using those compounds and compositions. Advantageously, it has been found that the N-substituted carbonyloxyalkylpyrrole compounds of the present invention, and compositions containing them, are effective insecticidal, acaricidal and molluscicidal agents for the control of insects, acarina and mollusks and for the protection of plants from attack by insects, acarina and mollusks. The compounds of the present invention are especially useful for the control of tobacco budworms.

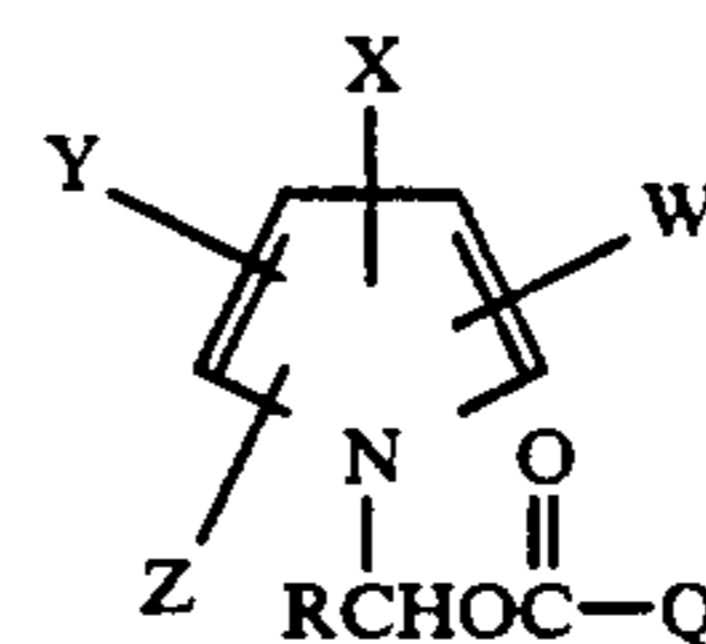
DETAILED DESCRIPTION OF THE INVENTION

Insects, acarina and mollusks destroy growing and harvested crops. In the United States alone, agronomic crops must compete with thousands of insect and acarid species. Accordingly, there is ongoing research to create new and more effective insecticides, acaricides and molluscicides for the control of insects, acarina and mollusks and for the protection of plants from attack by insects, acarina and mollusks. There is also ongoing research to create new insecticides and acaricides to overcome the resistance observed with several classes of insecticidal and acaricidal agents.

Advantageously, the present invention provides a method for controlling insects, acarina and mollusks by contacting said insects, acarina and mollusks, their breeding grounds, food supply or habitat with an insecticidally, acaricidally or molluscicidally effective amount of a formula I, N-substituted carbonyloxyalkylpyrrole compound.

The present invention also provides a method for protecting growing plants from attack by insects, acarina and mollusks by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally, acaricidally or molluscicidally effective amount of a formula I, N-substituted carbonyloxyalkylpyrrole compound.

The N-substituted carbonyloxyalkylpyrrole compounds of the present invention have the following structural formula I:



(I)

wherein

W is CN, NO₂, S(O)_nCF₂R₁ or



R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

n is an integer or 0, 1 or 2;

R₂ and R₃ are each independently hydrogen,

C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or
 phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF₃, CN, NO₂, S(O)_nCF₂R₁ or phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is halogen, CF₃ or phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF₃;
 R is hydrogen or C₁-C₄ alkyl;

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups,
 C₂-C₆ alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms,

CR₄R₅C(O)R₆, or
 CR₄R₅C(O)A;

R₄ and R₅ are each independently hydrogen,

C₁-C₆ alkyl optionally substituted with one or more halogen atoms,

C₁-C₆ alkoxy optionally substituted with one or more halogen atoms,

C₁-C₆ alkylthio optionally substituted with one or more halogen atoms,

phenyl optionally substituted with one or more halogen atoms,
 CN groups,
 NO₂ groups,
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms, or
 when R₄ and R₅ are taken together with the atom to which they are attached may form a C₃-C₆ cycloalkyl group optionally substituted with one to three C₁-C₄ alkyl groups, C₂-C₆ alkenyl groups or phenyl groups;

R₆ is

C₁-C₄ alkyl or phenyl optionally substituted with one or more halogen atoms,
 CN groups,
 NO₂ groups,
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

A is OR₆ or NR₇R₈; and

R₇ and R₈ are each independently hydrogen or C₁-C₄ alkyl.

Preferred N-substituted carbonyloxyalkylpyrrole compounds of the present invention are those wherein W is CN, NO₂, S(O)_nCF₂R₁ or



R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

n is an integer of 0, 1 or 2;

R₂ and R₃ are each independently hydrogen,

C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF₃, CN, NO₂, S(O)_nCF₂R₁ or phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is halogen, CF₃ or phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen, or CF₃;

R is hydrogen or C₁-C₄ alkyl; and

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or

phenyl groups optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

More preferred formula I insecticidal, acaricidal and molluscicidal agents are those wherein W is CN, NO₂, S(O)_nCF₂R₁ or



R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

n is an integer of 0, 1 or 2;

R₂ and R₃ are each independently hydrogen or C₁-C₄ alkyl optionally substituted with one or more halogen atoms;

X is Cl, Br, CF₃ or phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF₃ or phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is Cl, Br or CF₃;

R is hydrogen; and

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

Most preferred N-substituted carbonyloxyalkylpyrrole compounds of this invention which are especially effective insecticidal, acaricidal and molluscicidal agents are those wherein W is CN;

X is Cl, Br or phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br or CF₃;

Z is Cl or Br; and

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or

phenyl groups optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

Most preferred formula I insecticidal, acaricidal and molluscicidal agents are those wherein W is CN;

X is Cl, Br or phenyl optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br or CF₃;

Z is Cl or Br; and

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or

phenyl groups optionally substituted with one or more halogen atoms,
 NO₂ groups,
 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

phenyl groups optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

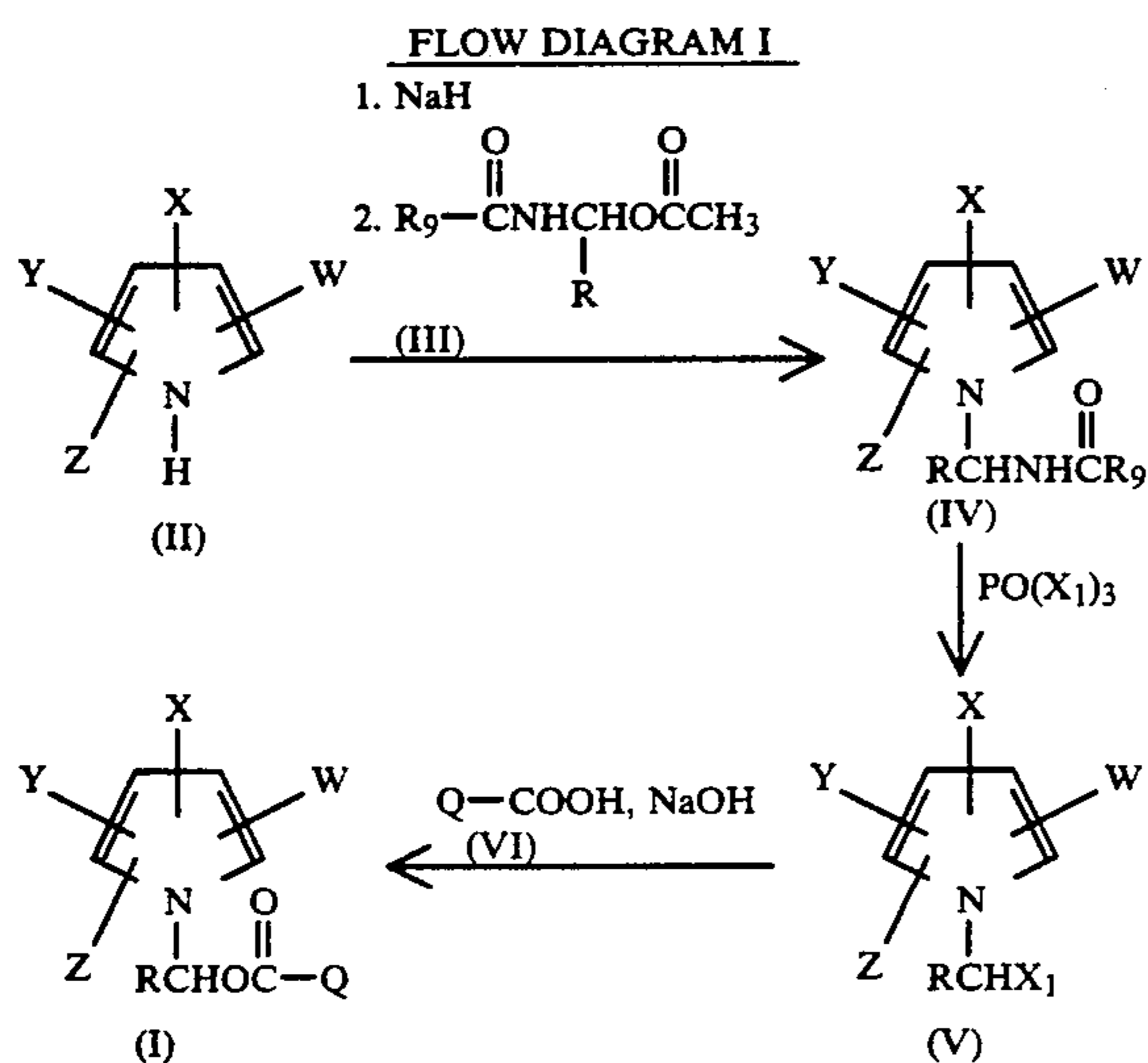
C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine.

Advantageously, it has been found that the formula I compounds of the present invention are especially useful for the control of tobacco budworms, southern armyworms, two-spotted spider mites and slugs.

Formula I compounds may be prepared as shown in Flow Diagram I.



wherein

R₉ is

C₁-C₆ alkyl optionally substituted with one to three halogen atoms,

phenyl optionally substituted with one or two halogen, CN, NO₂, C₁-C₄ alkyl, C₁-C₄ alkoxy or CF₃ groups,

2- or 3-thienyl or

2- or 3-furfuryl;

X₁ is Cl or Br; and

W, X, Y, Z, R and Q are as described hereinabove for formula I.

The appropriately substituted pyrroles of formula II is reacted with an alkylating agent of formula III in the presence of an alkali metal hydride or an alkali metal C-C₆ alkoxide to form an N-alkanoylaminoethyl or N-aroylethylaminomethylpyrrole of formula IV, said formula IV aminomethylpyrrole is then reacted with an excess of phosphorus oxychloride or phosphorus oxybromide to form a 1-halomethylpyrrole of formula V. Said 1-halomethylpyrrole is reacted with a carboxylic acid of formula VI in the presence of an alkali metal hydroxide, such as sodium or potassium hydroxide, to form desired N-substituted carbonyloxyalkylpyrrole compounds of formula I.

Starting formula II pyrrole compounds may be prepared according to the procedures described in U.S. Pat. No. 5,157,047 and U.S. patent application Ser. Nos. 392,495 filed on Aug. 11, 1989; 621,162 filed on Nov. 30, 1990; 776,967 filed on Oct. 15, 1991; 795,407 filed on Nov. 20, 1991; 803,289 filed on Dec. 4, 1991 and are

incorporated herein by reference thereto. Starting formula III alkylating agents are described in U.S. patent application Ser. No. 755,935 filed on Sept. 6, 1991 and is incorporated herein by reference thereto. In addition, certain formula V 1-halomethylpyrrole compounds wherein W is CN may be prepared as described in U.S. Pat. No. 5,118,816.

The N-substituted carbonyloxyalkylpyrrole compounds of the present invention are effective for controlling insects, acarina and mollusks. Those compounds are also effective for protecting growing or harvested crops from attack by insects, acarina and mollusks.

Insects controlled by the formula I compounds of this invention include Lepidoptera such as tobacco budworms, cabbage loopers, cotton boll worms, beet armyworms, southern armyworms and diamondback moths; Homoptera such as aphids, leaf hoppers, plant hoppers and white flies; Thysanoptera such as thrips; Coleoptera such as boll weevils, Colorado potato beetles, southern corn rootworms and mustard beetles; and Orthoptera such as locusts, crickets, grasshoppers and cockroaches. Acarine controlled by the compounds of this invention include mites such as two-spotted spider mites, carmine spider mites, banks grass mites, strawberry mites, citrus rust mites and leprosis mites. Mollusks controlled by the compounds of this invention include gastropoda such as snails, slugs, cowries and limpets. Advantageously, it has been found that the compounds of the present invention are especially effective against tobacco budworm eggs and third-instar larvae, southern armyworms, two-spotted spider mites and slugs.

In practice generally about 10 ppm to 10,000 ppm and preferably 100 ppm to about 5,000 ppm of a formula I N-substituted carbonyloxyalkylpyrrole compound, dispersed in water or another liquid carrier, is effective when applied to the plants, the crops or the soil in which said crops are growing to protect said crops from attack by insects, acarina and mollusks.

The formula I compounds of this invention are also effective for controlling insects, acarina and mollusks, when applied to the foliage of plants and/or to the soil or water in which said plants are growing in sufficient amount to provide a rate of from about 0.1 kg/ha to 4.0 kg/ha of active ingredient.

While the compounds of this invention are effective for controlling insects, acarina and mollusks when employed alone, they may also be used in combination with other biological chemicals, including other insecticides, acaricides and molluscicides. For example, the formula I compounds of this invention may be used effectively in conjunction or combination with pyrethroids, phosphates, carbamates, cyclodienes, endotoxin of bacillus thuringiensis (Bt), formamidines, phenol tin compounds, chlorinated hydrocarbons, benzoylphenyl ureas and the like.

The compounds of this invention may be formulated as emulsifiable concentrates, flowable concentrates, or wettable powders which are diluted with water or other suitable polar solvent, generally in situ, and then applied as a dilute spray. Said compounds may also be formulated in dry compacted granules, granular formulations, dusts, dust concentrates, suspension concentrates, microemulsions and the like all of which lend themselves to seed, soil, water and/or foliage applications to provide the requisite plant protection. Such formulations

include the compounds of the invention admixed with inert, solid or liquid diluents.

For example, wettable powders, dusts, and dust concentrate formulations can be prepared by grinding and blending together about 25% to about 85% by weight of formula I compounds and about 75% to about 15% by weight of a solid diluent such as bentonite, diatomaceous earth, kaolin, attapulgite, or the like, about 1% to 5% by weight of a dispersing agent such as sodium lignosulfonate, and about 1% to 5% by weight of a nonionic surfactant, such as octylphenoxy polyethoxy ethanol, nonylphenoxy polyethoxy ethanol or the like.

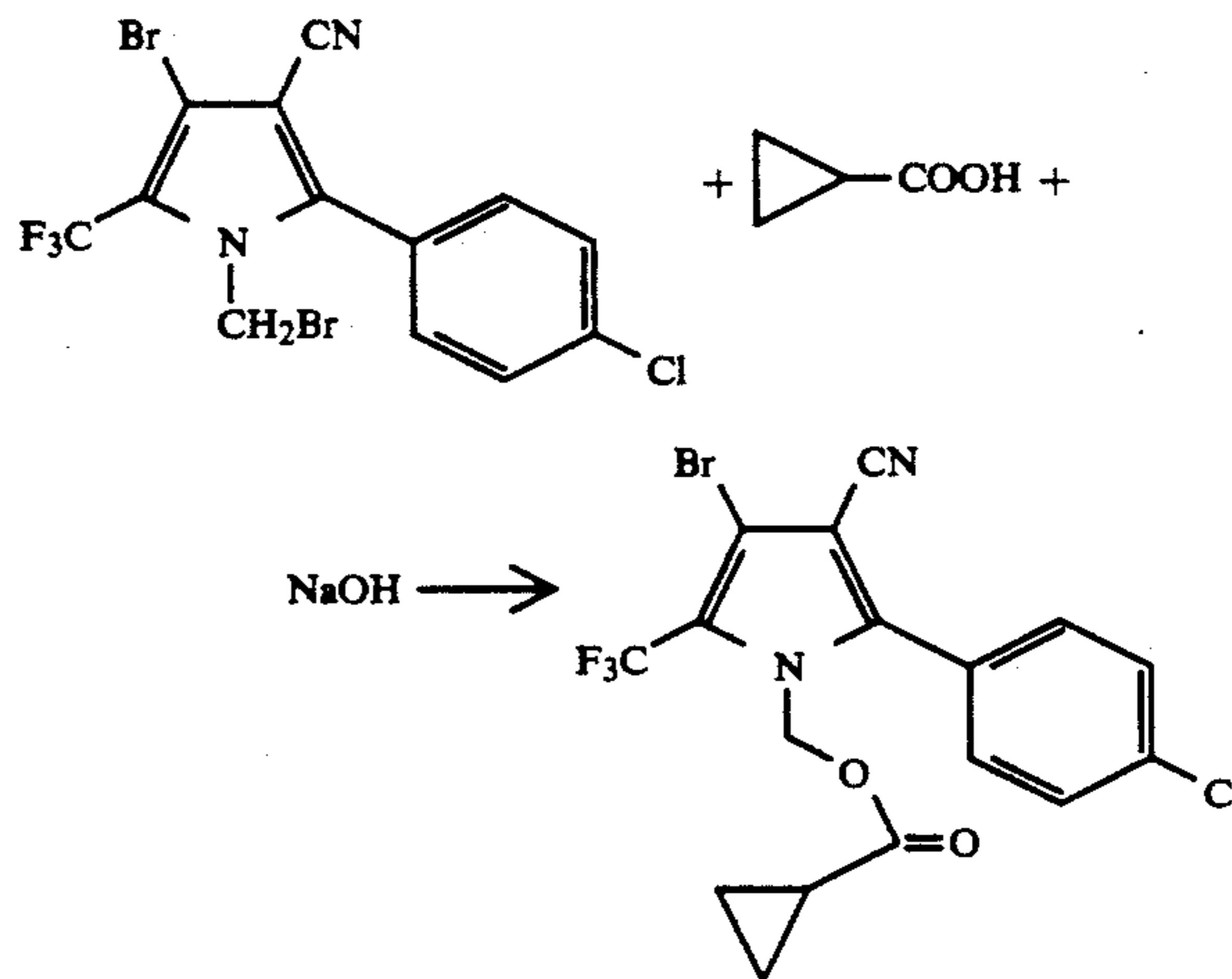
A typical emulsifiable concentrate can be prepared by dissolving about 15% to about 70% by weight of an N-substituted carbonyloxyalkylpyrrole compound in about 85% to about 30% by weight of a solvent such as isophorone, toluene, butyl cellosolve, methyl acetate, propylene glycol monomethyl ether, or the like and dispersing therein about 1% to 5% by weight of a nonionic surfactant such as an alkylphenoxy polyethoxy alcohol.

An especially effective method for controlling terrestrial gastropods with the formula I compounds of the invention, is to proffer the active molluscicidal material in the form of a bait formulation. These bait formulations can be widely varied but generally contain about 1% to 20% by weight of the active ingredient, about 40% to 50% by weight of a solid edible nutritive substance, about 5% to 10% by weight of a carbohydrate source such as sugar, molasses, corn syrup or the like and the remainder of the formulation, i.e. about 30% to 50% by weight of water or other consumable liquid.

In order to facilitate a further understanding of the invention, the following examples are presented to illustrate more specific details thereof. The invention is not to be limited thereby except as defined in the claims.

EXAMPLE 1

Preparation of
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate

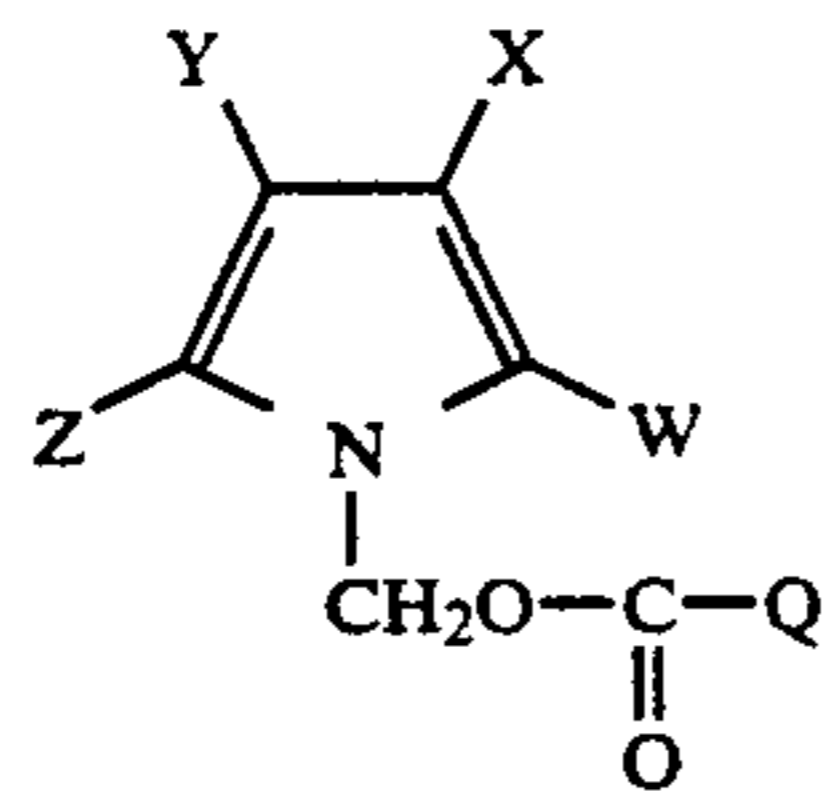


4-Bromo-1-(bromomethyl)-2-(p-chlorophenyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (2.21 g, 4.99 mmol) is added to a mixture of cyclopropanecarboxylic acid (0.52 g, 6.04 mmol) and sodium hydroxide (0.24 g, 6.0 mmol) in N,N-dimethylformamide. The reaction mixture is stirred overnight at room temperature, diluted with water and extracted with ethyl acetate. The combined organic extracts are washed sequentially with water and brine, dried over $MgSO_4$ and concentrated in vacuo to obtain a brown oil. The oil is triturated with hexanes to obtain an off white solid. Recrystallization of the solid from *n*-2-propanol gives the title product as tan needles (1.3 g, mp 122°–123° C.).

Using essentially the same procedure, but employing the appropriately substituted 1-(halomethyl)pyrrole and carboxylic acid, the following compounds are obtained:

| | | | | | | mp °C. |
|---|----|----|-----------------|---|-------------|--------|
| W | X | Y | Z | Q | | |
| | CN | Br | CF ₃ | | 120.0–121.5 | |
| | CN | Cl | CF ₃ | | 104–105 | |
| | CN | Cl | Cl | | 87–89 | |

-continued



| W | X | Y | Z | Q | mp °C. |
|----|----|----|-----------------|---|---------|
| | CN | Br | CF ₃ | | 90-91 |
| | CN | Br | CF ₃ | | 124-125 |
| | CN | Br | CF ₃ | | 51-56 |
| | CN | Cl | Cl | | 121-122 |
| Br | CN | Br | Br | | 105-106 |
| | CN | Cl | CF ₃ | | 105-106 |
| | Br | CN | Cl | | 96-97 |
| | CN | Cl | CF ₃ | | 156-158 |
| | CN | Cl | CF ₃ | | oil |

EXAMPLE 2

Insecticide and acaricide evaluations

The following tests show the efficacy of the compounds as insecticides and acaricides. The evaluations are conducted with solutions of test compounds dissolved or dispersed in 50/50 acetone/water mixtures. The test compound is technical material dissolved or dispersed in said acetone/water mixtures in sufficient

amounts to provide the concentrations set forth in Table I below.

All concentrations reported herein are in terms of active ingredient. All tests are conducted in a laboratory maintained at about 27° C. The rating system employed is as follows:

Rating System

0 = no effect

5 = 56-65% kill

-continued

| Rating System | |
|-----------------|-------------------|
| 1 = 10-25% kill | 6 = 66-75% kill |
| 2 = 26-35% kill | 7 = 76-85% kill |
| 3 = 36-45% kill | 8 = 86-99% kill |
| 4 = 46-55% kill | 9 = 100% kill |
| | — = no evaluation |

The test species of insects and acarina used in the present evaluations along with specific test procedures are described below.

Spodoptera eridania 3rd instar larvae, southern armyworm

A sieva lima bean leaf expanded to 7 to 8 cm in length is dipped in the test suspension with agitation for 3 seconds and placed in a hood to dry. The leaf is then placed in a 100×10 mm petri dish containing a damp filter paper on the bottom and 10 3rd instar caterpillars. The dish is maintained for 5 days before observations are made of mortality, reduced feeding or any interference with normal moulting.

Tetranychus urticae (OP-resistant strain), 2-spotted spider mite

Sieva lima bean plants with primary leaves expanded to 7 to 8 cm are selected and cut back to one plant per pot. A small piece is cut from a leaf taken from the main colony and placed on each leaf of the test plants. This is done about 2 hours before treatment to allow the mites to move over to the test plant and to lay eggs. The size of the cut piece is varied to obtain about 100 mites per leaf. At the time of the treatment, the piece of leaf used to transfer the mites is removed and discarded. The mite-infected plants are dipped in the test formulation for 3 seconds with agitation and set in the hood to dry. Plants are kept for 2 days before estimates of adult kill are made.

Empoasca abrupta, adults, western potato leafhopper

A Sieva lima bean leaf about 5 cm long is dipped in the test formulation for 3 seconds with agitation and placed in a hood to dry. The leaf is placed in a 100×10 mm petri dish containing a moist filter paper on the bottom. About 10 adult leafhoppers are added to each

dish and the treatments are kept for 3 days before mortality counts are made.

Heliothis virescens, 3rd instar tobacco budworm

Cotton cotyledons are dipped in the test formulation and allowed to dry in a hood. When dry, each is cut into quarters and ten sections placed individually in 30 mL plastic medicine cups containing a 5 to 7 mm long piece of damp dental wick. One 3rd instar caterpillar is added to each cup and a cardboard lid placed on the cup. Treatments are maintained for 3 days before mortality counts and estimates of reduction in feeding damage are made.

Heliothis virescens, tobacco budworm egg

Tobacco budworm eggs are collected on cheesecloth in the rearing colony. This cheesecloth is cut into 10 mm to 20 mm squares containing about 50-100 eggs per square. Each square is dipped in the test formulation and placed on a separate cotton cotyledon, previously dipped in the test formulation. The treatments are dried, transferred into an 8 ounce Dixie® cup (240 mL, 6 cm high, top diameter 9.5 cm, bottom diameter 8 cm) containing a 5 cm length of damp cotton dental wick and covered with a clear plastic lid. Treatments are maintained for three days before mortality counts are made.

Diabrotica undecimpunctata howardi, 3rd instar southern corn rootworm

One cc of fine talc is placed in a 30 mL wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. The jars are capped and the contents thoroughly mixed on a Vortex Mixer. Following this, ten 3rd instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the larvae. The treatments are held for 6 days before mortality counts are made. Missing larvae are presumed dead, since they decompose rapidly and can not be found. The concentration used in this test corresponds to approximately 50 kg/ha.

The data obtained for the above described evaluations are reported in Table I.

TABLE I

| Compound | Insecticide And Acaricide Evaluations | | | | | | | | | | |
|---|---------------------------------------|-----|----|----------------------|-----|------------------|----|-----------------|--------------|-----|--------------------------|
| | Southern Armyworm (ppm) | | | OP. Res. Mites (ppm) | | Leafhopper (ppm) | | Tobacco Budworm | | | S. Corn Rootworm (kg/ha) |
| | 1,000 | 100 | 10 | 300 | 100 | 100 | 10 | Egg (ppm) | Larvae (ppm) | 10 | 50 |
| [3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate | 9 | 9 | 9 | 9 | 9 | 9 | 5 | 0 | 9 | 8 | 9 |
| [3-Chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 7 | 9 | 9 | 9 |
| [2,3-Dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate | 9 | 9 | 9 | 9 | 9 | 9 | 0 | 0 | 9 | 6 | 0 |
| [3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 8 | 9 | 9 | 9 |
| [3-Bromo-5-(p-chloro- | 9 | 9 | 9 | 9 | 9 | 9 | 8 | 0 | 9 | 7.5 | 9 |

TABLE I-continued

| Compound | Insecticide And Acaricide Evaluations | | | | | | | | | | | |
|---|---------------------------------------|-----|----|----------------------------|-----|---------------------|----|---------------------------------|-----|-----|-----------------|--------------------------------|
| | Southern Armyworm (ppm) | | | OP. Res. Mites (ppm) | | Leafhopper (ppm) | | Tobacco Budworm Egg (ppm) | | | Larvae (ppm) | S. Corn Rootworm (kg/ha) |
| | 1,000 | 100 | 10 | 300 | 100 | 100 | 10 | 1,000 | 100 | 10 | 50 | |
| phenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl)methyl 1-phenylcyclopropanecarboxylate | 9 | 9 | 9 | 9 | 9 | 9 | — | 0 | 9 | 9 | 9 | |
| [3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl)methyl 1-methylcyclopropanecarboxylate | 9 | 9 | 9 | 5 | — | — | — | 0 | 9 | 6.5 | 0 | |
| [2,3-Dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl)methyl cyclohexanecarboxylate | 9 | 9 | 9 | 9 | 8 | — | — | 0 | 9 | 4 | 9 | |
| (2,3,5-Tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate | 9 | 5 | 0 | 9 | 0 | 3.5 | 0 | 9 | 0 | 0 | 0 | |
| [3-Chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl)methyl cyclobutanecarboxylate | 9 | 9 | 9 | 9 | 0 | 4.5 | 9 | 8 | 9 | 9 | 9 | |
| [3-Bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)pyrrol-1-yl)methyl cyclopropanecarboxylate | 9 | 9 | 7 | 9 | 8 | — | — | 0 | 9 | 0 | 5.7 | |
| [3-Chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl)methyl 1-(p-chlorophenyl)cyclopropanecarboxylate | 9 | 9 | 9 | 9 | 0 | — | — | 0 | 9 | 7 | 7.5 | |
| [3-Chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl)methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate | 9 | — | — | 0 | — | — | — | — | — | — | 0 | |

EXAMPLE 3

Evaluation of
(2,3,5-Tribromo-4-cyanopyrrol-1-yl)methyl
cyclopropanecarboxylate for the control of slugs,
species *Arion subfuscus*

The test compound is weighed and diluted in acetone to achieve the desired concentration, and 1.0 mL of each test solution is added to 0.65 g of unprocessed bran. The acetone is then removed by evaporation. The bait composition is prepared by mixing the above-said treated unprocessed bran with 0.35 mL of a 12% molasses solution. The thus-prepared bait composition is placed into the lid of a 1 oz jar which is then placed onto the bottom of an 8 oz waxed paper cup which has been lined with wet filter paper. Each cup is then infested with 8 slugs. A control cup which contains 0% test compound in the bait composition is also prepared and infested. Test treatments are examined daily for 6 days and feeding and mortality rates are recorded. The data obtained are reported below.

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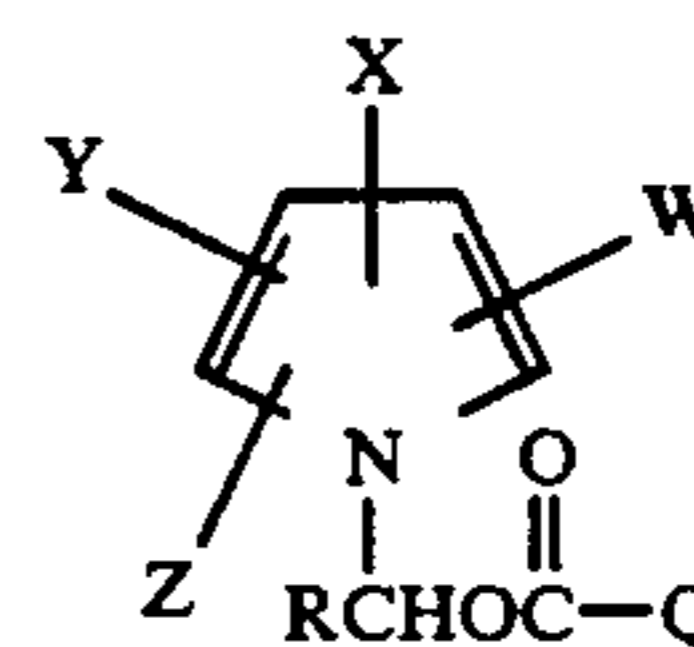
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| Compound | % Mortality of <i>Arion subfuscus</i> (% Bait) | | |
|---|--|------|-------|
| | 5.0% | 1.0% | 0.15% |
| (2,3,5-Tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate | 75 | 100 | 88 |

We claim:

1. A compound having the structural formula



wherein
W is CN, NO₂, S(O)_nCF₂R₁ or



R_1 is hydrogen, F, Cl, Br, CF_2H , CCl_2H , CCIFH , CF_3 or CCl_3 ; 5
 n is an integer of 0, 1 or 2;
 R_2 and R_3 are each independently hydrogen, 10
 C_1 - C_4 alkyl optionally substituted with one or more halogen atoms, or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, 15
 C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;
 X is halogen, CF_3 , CN, NO_2 , $\text{S}(\text{O})_n\text{CF}_2\text{R}_1$ or phenyl 20
optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1 - C_4 alkyl groups optionally substituted with one or 25
more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;
 Y is 30
halogen, CF_3 or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1 - C_4 alkyl groups optionally substituted with one 35
or more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;
 Z is hydrogen, halogen or CF_3 ;
 R is hydrogen or C_1 - C_4 alkyl; 40
 Q is 45
 C_3 - C_6 cycloalkyl optionally substituted with one or more C_1 - C_6 alkyl groups, C_2 - C_6 alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1 - C_4 alkyl groups optionally substituted with one 50
or more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms,
 $\text{CR}_4\text{R}_5\text{C}(\text{O})\text{R}_6$, or
 $\text{CR}_4\text{R}_5\text{C}(\text{O})\text{A}$;
 R_4 and R_5 are each independently hydrogen, 55
 C_1 - C_6 alkyl optionally substituted with one or more halogen atoms, C_1 - C_6 alkoxy optionally substituted with one or more halogen atoms, C_1 - C_6 alkylthio optionally substituted with one or 60
more halogen atoms, phenyl optionally substituted with one or more halogen atoms, CN groups, NO_2 groups, C_1 - C_4 alkyl groups optionally substituted with one or 65
more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms, or

when R_4 and R_5 are taken together with the atom to which they are attached may form a C_3 - C_6 cycloalkyl group optionally substituted with one to three C_1 - C_4 alkyl groups, C_2 - C_6 alkenyl groups or phenyl groups;
 R_6 is
 C_1 - C_4 alkyl or phenyl optionally substituted with one or more halogen atoms, CN groups, NO_2 groups, C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;
 A is OR_6 or NR_7R_8 ; and
 R_7 and R_8 are each independently hydrogen or C_1 - C_4 alkyl.
2. The compound according to claim 1 wherein Q is C_3 - C_6 cycloalkyl optionally substituted with one or more C_1 - C_6 alkyl groups, C_2 - C_6 alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms.
3. The compound according to claim 2 wherein R_2 and R_3 are each independently hydrogen or C_1 - C_4 alkyl optionally substituted with one or more halogen atoms;
 X is Cl, Br, CF_3 or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;
 Y is Cl, Br, CF_3 or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;
 Z is Cl, Br or CF_3 ; and
 R is hydrogen.
4. The compound according to claim 3 wherein W is CN;
 X is Cl, Br or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;
 Y is Cl, Br, or CF_3 ; and
 Z is Cl or Br.
5. The compound according to claim 4 [3-chloro-5-(phlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate.

6. The compound according to claim 4 [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate.

7. The compound according to claim 4 [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate.

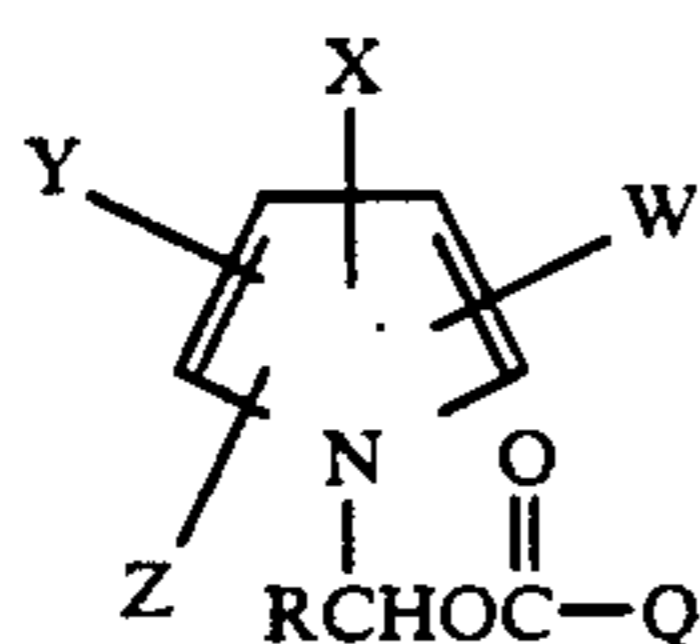
8. The compound according to claim 4 [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate.

9. The compound according to claim 4 [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate.

10. The compound according to claim 4 [2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate.

11. The compound according to claim 4 (2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate.

12. A method for controlling insects, acarina and mollusks which comprises contacting said insects, acarina and mollusks their breeding ground, food supply or habitat with an insecticidally, acaricidally or molluscicidally effective amount of a compound having the structural formula



wherein

W is CN, NO₂, S(O)_nCF₂R₁ or



R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

n is an integer of 0, 1 or 2;

R₂ and R₃ are each independently hydrogen,

C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF₃, CN, NO₂, S(O)_nCF₂R₁ or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is halogen, CF₃ or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF₃;

R is hydrogen or C₁-C₄ alkyl;

Q is

C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms,

CR₄R₅C(O)R₆, or

CR₄R₅C(O)A;

R₄ and R₅ are each independently hydrogen,

C₁-C₆ alkyl optionally substituted with one or more halogen atoms,

C₁-C₆ alkoxy optionally substituted with one or more halogen atoms,

C₁-C₆ alkylthio optionally substituted with one or more halogen atoms,

phenyl optionally substituted with one or more halogen atoms,

CN groups,

NO₂ groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms, or

when R₄ and R₅ are taken together with the atom to which they are attached may form a C₃-C₆ cycloalkyl group optionally substituted with one to three C₁-C₄ alkyl groups, C₂-C₆ alkenyl groups or phenyl groups;

R₆ is C₁-C₄ alkyl or phenyl optionally substituted with one or more halogen atoms,

CN groups,

NO₂ groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

A is OR₆ or NR₇R₈; and

R₇ and R₈ are each independently hydrogen or C₁-C₄ alkyl.

13. The method according to claim 12 wherein

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

14. The method according to claim 13 wherein

R₂ and R₃ are each independently hydrogen or C₁-C₄ alkyl optionally substituted with one or more halogen atoms;

X is Cl, Br, CF₃ or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF₃ or phenyl optionally substituted with one or more halogen atoms;

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is Cl, Br or CF₃; and

R is hydrogen.

15. The method according to claim 14 wherein

W is C_n;

X is Cl, Br or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, or CF₃; and

Z is Cl or Br.

16. The method according to claim 15 wherein the compound is selected from the group consisting of [3-

chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)-pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-

bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)-pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate;

[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate;

[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;

(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate;

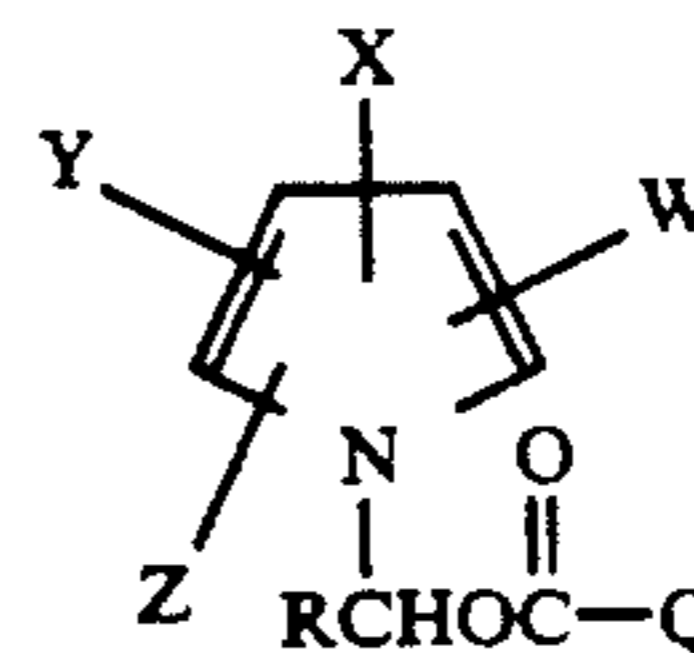
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate;

[3-bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)-pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; and

[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate.

17. A method for protecting growing plants from attack by insects, acarina and mollusks which comprises applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally, acaricidally or molluscicidally effective amount of a compound having the structural formula



wherein W, X, Y, Z, R and Q are as described in claim 11.

18. The method according to claim 17 wherein Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

19. The method according to claim 18 wherein R₂ and R₃ are each independently hydrogen or C₁-C₄ alkyl optionally substituted with one or more halogen atoms;

X is Cl, Br, CF₃ or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF₃ or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is Cl, Br or CF₃; and

R is hydrogen.

20. The method according to claim 19 wherein

W is C_n;

X is Cl, Br or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, or CF₃; and

Z is Cl or Br.

21. The method according to claim 20 wherein the compound is selected from the group consisting of [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)-pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;

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[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate;

[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluorop-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate;

[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluorop-tolyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;

(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate;

[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate;

[3-bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; and

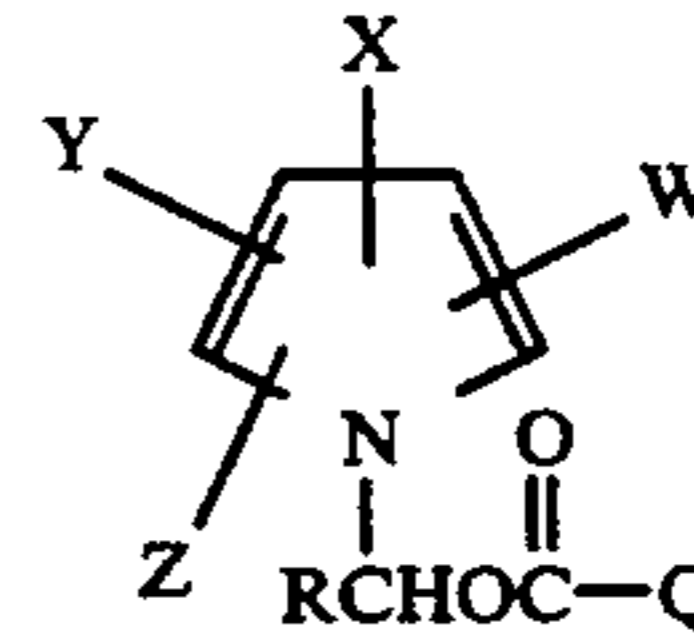
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate.

22. The method according to claim 17 wherein the compound is applied to the plants or soil in which they are growing at a rate of about 0.100 kg/ha to 4.0 kg/ha.

23. A composition for controlling insects, acarina and mollusks comprising an agronomically acceptable car-

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rier and an insecticidally, acaricidally or molluscicidally effective amount of a compound having the structural formula



wherein W, X, Y, Z, R and Q are as described in claim 12.

24. The composition according to claim 23 wherein Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms, NO₂ groups, CN groups, C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

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